

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

* * * * *

CHEMICAL-MECHANICAL POLISHING METHODS

* * * * *

Michael T. Andreas

ATTORNEY'S DOCKET NO. MI22-1229

EL844053658

1 CHEMICAL-MECHANICAL POLISHING METHODS

2

3 TECHNICAL FIELD

4 This invention relates to chemical-mechanical polishing methods.

5

6 BACKGROUND OF THE INVENTION

7 Chemical-mechanical polishing (CMP), also known as chemical-
8 mechanical planarization, is widely used in a variety of industries,
9 including the semiconductor processing industry. CMP can remove
10 unwanted material from a substrate, planarize a substrate, and/or create
11 a desired finish on a substrate. All of such intentions may be
12 generically termed "polishing." Generally, the technology involves
13 pressing some sort of solid abrasive material against the substrate to
14 accomplish the polishing and/or planarization. The solid abrasive
15 material may be applied in a CMP slurry of such material and liquid
16 carriers and/or chemically active components as desired. Alternatively,
17 abrasive material may be carried within a polishing pad. Still other
18 techniques are encompassed within the technology.

19 One common byproduct of CMP is that abrasive material residues
20 often remain on the substrate. In some applications, residual abrasive
21 material can negatively influence subsequent processing and/or result in
22 defective products. Accordingly, a variety of approaches have been
23 attempted to resolve the problem of residual abrasive material.

1 One conventional approach is to use hydrofluoric acid-based
2 chemistries to undercut particles attached to a silicon oxide substrate.
3 A problem with hydrofluoric acid-based chemistries is that microscratches
4 formed in the substrate as a result of CMP may be aggravated in the
5 acidic conditions. Further, insoluble fluoride compounds may be formed
6 from reactions of hydrofluoric acid with the abrasive material.

7 Another conventional approach includes application of ammonium
8 hydroxide or tetramethylammonium hydroxide (TMAH) to disperse
9 residual abrasive material. At a high pH, a silicon oxide surface and
10 most abrasive material particles, including ceria, alumina, and silica
11 exhibit a negative surface charge. Such charge characteristics provide
12 electrostatic repulsion. Experimentally, such a method has produced
13 limited benefits and appears to work much better for aluminum oxide
14 particles in comparison to cerium oxide particles.

15 Still another conventional technique involves etching and/or
16 dissolution of abrasive particles. For cerium oxide particles, such may
17 be accomplished with the application of a mixture of hydrogen peroxide
18 and sulfuric acid. While this method exhibits some effectiveness
19 experimentally, it is incompatible with any surface structures featuring
20 exposed metal.

21 Accordingly, it is desired to provide a new method for removing
22 CMP residual abrasive material from a substrate.

1 **SUMMARY OF THE INVENTION**

2 In accordance with an aspect of the invention, a chemical-
3 mechanical polishing (CMP) method includes applying a solid abrasive
4 material to a substrate, polishing the substrate, flocculating at least a
5 portion of the abrasive material, and removing at least a majority portion
6 of the flocculated portion from the substrate. Such a method can
7 include polishing with a CMP slurry or polishing pad. It may further
8 include applying a surfactant-comprising material to the substrate to assist
9 in effectuating flocculation of the abrasive material. Such surfactant
10 comprising material may be cationic which includes, for example, a
11 quaternary ammonium substituted salt. Also, for example, the
12 surfactant-comprising material may be applied during polishing, brush
13 scrubbing, pressure spraying, or buffing.

14 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

16 This disclosure of the invention is submitted in furtherance of the
17 constitutional purposes of the U.S. Patent Laws "to promote the progress
18 of science and useful arts" (Article 1, Section 8).

19 One aspect of the present invention provides a chemical-mechanical
20 polishing (CMP) method which involves applying a solid abrasive material
21 to a substrate. Such substrate can include a semiconductor substrate.
22 In the context of this document, the term "semiconductor substrate" or
23 "semiconductive substrate" is defined to mean any construction comprising

1 semiconductive material, including, but not limited to, bulk
2 semiconductive materials such as a semiconductive wafer (either alone or
3 in assemblies comprising other materials thereon), and semiconductive
4 material layers (either alone or in assemblies comprising other materials).
5 The term "substrate" refers to any supporting structure, including, but
6 not limited to, the semiconductive substrates described above.

7 Applying a solid abrasive material can include applying a CMP
8 slurry of substantially dispersed, solid abrasive material or applying a
9 polishing pad comprising solid abrasive material. A variety of CMP
10 slurries and polishing pads are conceivable that can include a variety of
11 components. Examples of solid abrasive material include cerium oxide,
12 aluminum oxide, mixtures thereof, and combinations thereof with other
13 materials. Preferably, the solid abrasive material comprises ceria.
14 Accordingly, ceria-based abrasive material is also preferred. The solid
15 abrasive material may be substantially dispersed within the CMP slurry,
16 that is, the solid abrasive material is not entirely agglomerated into
17 floccule comprising multiple solid abrasive particles. Depending on the
18 application, some agglomeration of abrasive material particles may be
19 tolerated. However, substantial dispersion alleviates the problem of
20 unnecessary scratching or other similar damage to a substrate from
21 oversized floccule.

22 The method next comprises polishing the substrate. The
23 parameters under which such polishing is to occur may be established

1 according to the knowledge of those skilled in the technology at the
2 time the method is being practiced. That is, it is contemplated that the
3 present method is applicable both to currently available CMP parameters
4 as well as others that may be later developed.

5 The method further includes flocculating at least a portion of the
6 abrasive material on the substrate. Such flocculating may occur by a
7 variety of means and at a variety of points within the CMP method.
8 One means for flocculating abrasive material includes applying a
9 surfactant comprising material. A variety of surfactant comprising
10 materials are suitable and may be characterized in a variety of ways.

11 One such suitable surfactant comprising material exhibits the
12 characteristic of decreasing a settling time for the abrasive material in
13 an aqueous dilution of the slurry. The CMP slurry may be diluted in
14 water, such as de-ionized water, to produce an aqueous dilution of the
15 CMP slurry having a desired concentration of the CMP slurry. For
16 example, the aqueous dilution may comprise 0.1 weight percent (wt%)
17 CMP slurry, 1 wt% slurry, or some other dilution level. The aqueous
18 dilution of the CMP slurry will exhibit a settling time. That is, after
19 a desired amount of time passes, analysis can be conducted to determine
20 the extent to which solid abrasive particles have settled within the
21 aqueous dilution. For example, analysis could occur on 24-hour cycles,
22 or some other duration.

Settling time may vary depending upon a variety of factors, including the dilution level of the CMP slurry (i.e. initial particle concentration in the dilution), pH, and the temperature of the aqueous dilution. It is expected that the most significant decreases in settling time compared to an aqueous dilution without a surfactant comprising material will occur when the temperature of the aqueous dilution does not exceed about 40 °Celsius (°C). A variety of settling times may also be used to measure the effectiveness of a surfactant comprising material. One example of a settling time is the elapsed time beginning from the mixing of a surfactant comprising material with the aqueous dilution up to the time when a designated percentage of the abrasive material has settled from the supernatant of the aqueous dilution. Settling time is considered to decrease if such elapsed time is less for a dilution with the surfactant comprising material.

Another way to characterize settling time is to compare the percentage of abrasive material that has settled from an aqueous dilution of the slurry after a set amount of time, for example, 24 hours. Settling time after addition of a surfactant comprising material is considered to decrease if an increased percentage of abrasive material settles from the supernatant in an aqueous dilution after a designated amount of time passes.

In another aspect of the present invention, a suitable surfactant comprising material exhibits a 1-hour settling rate constant of greater

than 0.035 for the abrasive material in an aqueous mixture of about 0.1 wt% surfactant and about 1 wt% CMP slurry containing 3 wt% abrasive material. Alternatively, the settling rate constant may be greater than about 0.09. As indicated above in the discussion on settling time, it may be that the desired 1-hour settling rate constant is achieved when the temperature of the aqueous mixture does not exceed about 40° C. Settling rate constant may be calculated using the following equation:

$$k = \frac{1}{t} \ln\left(\frac{c_0}{c_t}\right)$$

Wherein k is the settling rate constant, t is elapsed time, c_0 is the initial concentration, and c_t is concentration at elapsed time t. Accordingly, in calculating the 1-hour settling rate constant, t = 1 hour, c_0 = initial concentration of abrasive material in the supernatant of the about 1 wt% slurry dilution and c_t = the concentration of abrasive material in the aqueous dilution after one hour.

The weight percent of abrasive material in the CMP slurry may be known and initial concentration can be calculated given the dilution comprises about 1 wt% slurry. However, improved accuracy in determining settling rate constant is expected when initial concentration is determined by analysis rather than by calculation. Inductively coupled plasma optical emission spectrometry (ICP-OES) is one suitable analysis technique. Other techniques may also be used, such as gravimetric standard methods for determination of percent solids, however, they may

1 be less preferable. Using ICP-OES, the weight percent of a particular
2 metal, such as aluminum or cerium, is determined from the analytical
3 technique and may often be equated with a concentration of abrasive
4 material at a particular time. That is, instead of determining the actual
5 concentration of abrasive material as a whole, the concentration of a
6 tracer material, such as aluminum or cerium, may be determined.
7 Generally, a decrease in the concentration of the tracer material will be
8 proportional to a decrease in the concentration of the abrasive material.

9 In another aspect of the present invention, a suitable surfactant
10 comprising material may be characterized by its inclusion of particular
11 surfactants. For example, the surfactant may be cationic. Cationic
12 surfactants that are particularly suitable include quaternary ammonium
13 substitute salts, such as a quaternary ammonium halide. Specific suitable
14 surfactants include cetyltrimethylammonium bromide (available as
15 Rhodaquat --242B/99 from Ashland Chemical Co. in Dublin, Ohio) and
16 polyethoxylated quaternary ammonium halide. Examples of
17 polyethoxylated quaternary ammonium halide compounds include
18 ethoxylated stearyl methyl quaternary ammonium chloride and ethoxylated
19 cocoalkyl methyl quaternary ammonium chloride. The two compounds
20 are available as, respectively, Ethoquad 18/25 and Ethoquad C/25 from
21 Akzo Nobel Surface Chemistry Inc. in Stratford, Connecticut. Of course,
22 given the variety of ways in which a suitable surfactant may be
23 characterized, it is expected that other compounds may also be suitable.

1 The concentration of the surfactant in the surfactant comprising material
2 can be, for example, about 10 micrograms per milliliter ($\mu\text{g}/\text{ml}$) to about
3 10,000 $\mu\text{g}/\text{ml}$. Alternatively, the surfactant concentration can comprise
4 about 100 $\mu\text{g}/\text{ml}$ to about 1,000 $\mu\text{g}/\text{ml}$.

5 As indicated, the flocculation may occur under a variety of
6 conditions, but preferably when the temperature of the substrate does not
7 exceed about 40° C. Such temperature limit has been approximated as
8 a point below which improved flocculation is expected. Nevertheless, it
9 is also contemplated that such temperature limit may vary with respect
10 to a particular surfactant, abrasive material, and/or substrate, among
11 other factors. The flocculating can further comprise complexing at least
12 a portion of the abrasive material with a surfactant. Such complexing
13 may in turn form floccule. The formation of floccule is one mechanism
14 contemplated by the present invention by which settling time may be
15 decreased and an appropriate one-hour settling rate constant may be
16 achieved.

17 As suggested earlier, the flocculating can occur after the polishing.
18 In one aspect of the present invention, it is contemplated that primary
19 polishing of the substrate may be followed by buffing the substrate along
20 with applying a surfactant comprising material and flocculating at least
21 a portion of the abrasive material. Primary polishing can include
22 polishing with a CMP slurry or a polishing pad comprising solid abrasive
23 material. Buffing can be less aggressive, that is, use a softer polishing

1 pad, abrasive material that is less abrasive, and/or less chemically active
2 polishing media. Buffing may occur on a secondary platen of a CMP
3 tool as opposed to a primary platen where primary polishing often
4 occurs. In some contexts, buffing can be considered part of polishing.
5 Thus, flocculating can also occur during polishing.

6 One potential concern of applying surfactant comprising material
7 during a polishing and/or buffing step is that flocculated particles may
8 produce undesirable scratches or other defects in a substrate. The
9 tendency for such scratches and/or defects to form tends to decrease as
10 the down-force of a polishing surface on a substrate is reduced. Often,
11 the down-force of a polishing surface is less during a buffering step than
12 during a primary polishing step. Accordingly, applying a surfactant
13 comprising material can be conducted during a buffering step, and perhaps
14 another low down-force or lesser aggressive polishing step. Of course,
15 the ability to apply surfactant comprising material during such steps may
16 be influenced by the hardness of abrasive material and/or the substrate
17 being polished or buffed. The softer the substrate and the harder the
18 abrasive material, the more it is likely that scratches or defects may
19 result.

20 A CMP method according to the present invention further includes
21 removing at least a majority portion of the flocculated portion of the
22 abrasive material from the substrate. Such removal may be accomplished
23 by a variety of means and at a variety of points in a CMP method after

1 flocculation of abrasive material. Accordingly, in one aspect, brush
2 scrubbing the substrate using a scrubbing solution comprising a surfactant
3 material to flocculate abrasive material can remove at least a majority
4 portion of the abrasive material. Brush scrubbing may be performed
5 with a polyvinyl alcohol (PVA) brush. In another aspect, pressure
6 spraying the substrate using a spray solution comprising a surfactant
7 material to flocculate abrasive material can remove at least a majority
8 portion of the abrasive material. Flocculation may also be performed by
9 immersion in an aqueous bath comprising the surfactant material. Of
10 course, it is contemplated that flocculation and/or removal of abrasive
11 material may occur at yet other points in a CMP method. High-pressure
12 spray action may further be used to clean the floccule from the
13 substrate.

EXAMPLE

Aqueous dilutions of the thirteen surfactants listed in Table 1 were prepared at 0.1 wt% concentration using a heat/stir plate and de-ionized water. As mixed, Hitachi shallow trench isolation (STI) slurry containing a ceria abrasive material for CMP was added at approximately 1 wt% loading to form an aqueous dilution of the slurry with each of the thirteen surfactants. The Hitachi STI slurry was also added to de-ionized water at approximately 1 wt% loading as a control. An additional thirteen slurry dilutions with surfactant and one de-ionized water control were prepared using aged, mixed Rodel tungsten CMP

(WCMP) slurry containing alumina abrasive material, instead of the Hitachi slurry. Approximately 15 hours after initial preparation, the dilutions were agitated to simulate initial conditions and an approximately 1 ml sample of the supernatant of each solution was diluted 100 to 1 in de-ionized water. The diluted sample was analyzed by ICP-OES with a Varian Liberty 110 unit using a standard V-groove nebulizer and polypropylene spray chamber. Emission spectra were referenced to National Institute of Standards and Technology (NIST) traceable aluminum and cerium calibration standards. Samples were taken and analyses repeated each day for three days, on the seventh day, and on the thirteenth day following the initial agitation. Using the ICP-OES analyses, ceria and alumina concentrations of the aqueous dilutions were calculated and are presented, respectively, in Tables 2 and 3 below. For samples showing visible solids precipitation and an undetectable level of metal content, suspended solids were estimated to be 0 wt%.

1 Table 1: Experimental Surfactants.

Supplier	Surfactant	Description
Air Products	CT-131	anionic/nonionic dispersant
	CT-141	anionic dispersant
	CT-324	wetting agent/dispersant
Akzo Nobel	Ethoquad 18/25	ethoxylated stearyl methyl quaternary ammonium chloride
	Ethoquad C/25	ethoxylated cocoalkyl methyl quaternary ammonium chloride
Ashland	Alkamuls PSMO-20	ethoxylated (20) sorbitan monooleate
	Antarox P-104	ethoxylated polyoxypropylene
	Igepal DM-710	ethoxylated dinonylphenol/ nonophenol (branched)
	Rhodafac RE-610	polyoxyethylene (branched) nonylphenyl ether phosphate
	Rhodaquat M-242B/99	cetyltrimethyl ammonium bromide
BYK-Chemie	Anti Terra U80	unsaturated polyamine amide polymer acid salt, 2-butoxyethanol, xylene (dispersant blend)
Uniqema	Renex 30	ethoxylated C ₁₁ -C ₁₄ isoalcohols (wetting agent)
	Renex 36	ethoxylated C ₁₁ -C ₁₄ isoalcohols (wetting agent)

Table 2: %Ceria Results

Surfactant	0 hrs.	26 hrs.	50 hrs.	75 hrs.	170 hrs.	316 hrs.
Control	1.11	0.85	0.65	0.63	0.56	0.51
CT-131	1.15	0.73	0.60	0.57	0.55	0.45
CT-141	1.09	0.51	0.52	0.47	0.45	0.40
CT-324	1.10	0.23	0.60	0.53	0.43	0.40
EQ-18/25	0.65	0.08	0.00	0.00	0.00	0.00
EQ-C/25	0.72	0.09	0.00	0.00	0.00	0.00
PSMO-20	1.10	0.83	0.61	0.59	0.52	0.47
P-104	1.05	0.29	0.63	0.59	0.48	0.46
DM-710	1.07	0.36	0.56	0.49	0.43	0.42
RE-610	0.86	0.33	0.25	0.22	0.24	0.18
M-242B/99	0.03	0.03	0.00	0.00	0.00	0.00
AT-U80	1.10	0.35	0.44	0.40	0.33	0.30
RX-30	1.11	0.70	0.60	0.49	0.43	0.40
RX-36	1.08	0.65	0.59	0.55	0.42	0.40

Table 3: %Alumina Results

Surfactant	0 hrs.	27 hrs.	51 hrs.	75 hrs.	170 hrs.	317 hrs.
Control	1.09	0.14	0.12	0.13	0.00	0.00
CT-131	1.16	0.50	0.41	0.32	0.25	0.19
CT-141	1.19	0.67	0.50	0.40	0.29	0.21
CT-324	1.11	0.08	0.07	0.07	0.00	0.00
EQ-18/25	1.04	0.56	0.36	0.28	0.21	0.14
EQ-C/25	1.04	0.38	0.20	0.18	0.00	0.00
PSMO-20	1.16	0.18	0.15	0.15	0.00	0.00
P-104	1.10	0.20	0.16	0.16	0.00	0.00
DM-710	1.23	0.18	0.15	0.15	0.00	0.00
RE-610	1.15	0.94	0.82	0.76	0.59	0.55
M-242B/99	1.06	0.65	0.48	0.40	0.25	0.20
AT-U80	0.61	0.38	0.31	0.26	0.21	0.15
RX-30	1.10	0.16	0.15	0.14	0.00	0.00
RX-36	1.18	0.86	0.69	0.40	0.39	0.28

The results of ceria settling for the Hitachi STI slurry are summarized in Table 2. The ceria control dilution showed minimal settling relative to all experimental solutions over the thirteen day period.

Such may be due to the ingredients of the Hitachi STI slurry that encourage dispersal of ceria abrasive material and, thus, discourage settling. Notably, some surfactants caused ceria to settle much faster than the control. In particular, both Ethoquads (EQ-18/25 and EQ-C/25) and Rhodaquat (M-242B/99) caused such rapid settling that agitation did not restore the original (as-prepared) ceria concentration. Accordingly, the ceria concentration indicated for time 0 is much less than the approximate 1 wt% loading of the other dilutions. These three surfactants are cationic and are the only quaternary ammonium salts among the thirteen surfactants.

Some of the dilutions showed the strange effect of initially dropping in ceria concentration, then increasing in concentration, and then dropping again. This is typical of oscillating chemical reactions governed by the kinetics of two competing equilibria. Some other solutions showed minimal difference in settling as compared to the control. Only the three quaternary ammonium salts produced complete settling of ceria by completion of the thirteen day trial.

The results of alumina settling are summarized in Table 3. The alumina in the Rodel WCMP slurry dilution without a surfactant (the control dilution) settled quickly. Approximately 90% of the initial alumina settled within 24 hours. Most of the surfactants had little effect on alumina settling compared to the control dilution, suggesting minimal interaction. Some surfactants showed moderate dispersion of alumina,

1 reducing the degree of settling compared to the control dilution with 20-
2 30 wt% of the initial alumina remaining after thirteen days. One
3 surfactant, Rhodafac (RE-610), provided enough dispersion to keep
4 approximately 50% of the original alumina dispersed after thirteen days.
5 Rhodafac is an anionic surfactant and the only phosphate among the
6 thirteen surfactants.

7 Using setup conditions and the first three days of settling data,
8 first order settling rate constants were calculated using the equation set
9 forth above and a one-hour settling rate constant was determined for
10 each surfactant as applied to both ceria and alumina. The one-hour
11 settling rate constants are listed in Table 4 below. Notably, the higher
12 settling rate constants correspond to higher settling rates. As expected,
13 the two Ethoquads and Rhodaquat exhibited the highest settling rate
14 constants for ceria abrasive material.

15

16

17

18

19

20

21

22

23

1 Table 4: Settling Rate Constants (1-hour)

2 Surfactant	3 Ceria	4 Alumina
3 Control	0.010	0.051
4 PSMO-20	0.011	0.046
5 CT-131	0.013	0.024
6 RX-30	0.014	0.048
7 RX-36	0.015	0.013
8 CT-141	0.020	0.018
9 DM-710	0.023	0.046
10 P-104	0.025	0.044
11 AT-U80	0.026	0.030
12 CT-324	0.028	0.065
13 RE-610	0.033	0.008
14 EQ-C/25	0.098	0.035
15 EQ-18/25	0.102	0.024
16 M-242B/99	0.136	0.018

11 In compliance with the statute, the invention has been described
12 in language more or less specific as to structural and methodical
13 features. It is to be understood, however, that the invention is not
14 limited to the specific features shown and described, since the means
15 herein disclosed comprise preferred forms of putting the invention into
16 effect. The invention is, therefore, claimed in any of its forms or
17 modifications within the proper scope of the appended claims
18 appropriately interpreted in accordance with the doctrine of equivalents.